Optical Coherence and Anisotropy Studies of the First Events in Photosynthesis

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Abstract: Femtosecond optical coherence and anisotropy measurements are reported for the photosynthetic reaction center (*Rb. Sph*) revealing rapid electronic dephasing of both P* and B*, and novel polarization responses.

Although much work has focused on the dynamics prior to and during charge separation in the photosynthetic reaction center,[1,2,3,4] many issues remain unresolved, including: (1) the spectrum of fluctuations (frequencies, couplings...) that describes the interaction of the reaction center chromophores with the protein environment, and (2) what is the influence of the upper excitonic state of the special pair (P_{y+}) in energy and electron transfer. In this report, we present the results of optical coherence[5,6,7,8] (photon echo) and anisotropy measurements[9] of the photosynthetic reaction center of Rhodobactor Sphaeroides at room temperature. All experiments are conducted with a home-built cavity dumped Ti:Al_2O_3 laser that is tunable across the near IR absorption bands of the RC.

The two-pulse photon echo responses have been detected for the photosynthetic cofactors, P and accessory bacteriochlorophyll$_a$ B, and BChl$_a$ monomers in solution[10,11]. These echos all show intermediate shifts from t=0 of 8-12 fs, and exponential decays. Utilizing the Bloch analysis approach, and incorporating hole burning parameters for inhomogeneous broadening, the echos are all found to be in the "homogeneous" limit with T_2 times of 20, 23, and 26 fs for B, P, and BChl monomers, respectively. The homogeneous linewidth extracted from the optical dephasing for P agrees reasonably with extrapolations of temperature dependent hole burning studies.[12,13] Stimulated (3-pulse) photon echo results reveal that spectral diffusion occurs on a 700 fs timescale, indicating that inhomogeneous broadening (i.e. slow bath fluctuations) is also contributing to the echos. The two pulse echo for B is shown in figure 1, as well as the simulated result obtained using the spectral density shown in figure 1b. The spectral density includes contributions from inhomogeneous broadening, intramolecular vibrations (dephasing times and displacements obtained from pump probe and Raman[14] spectroscopy) and a broad "phonon" bath component. This spectral density also provides an excellent fit to the linear absorption spectra, but must be modified to fit the 3PE data, probably to account for dynamical energy transfer processes.

To further characterize the dynamical response of the system to optical excitation, the optical anisotropy was measured as a function of both excitation wavelength (using a spectrally narrowed pump pulse) and detection wavelength (broadband probe). The contributions to the optical signals are analyzed based on their spectral and polarization responses. Four distinct features are consistently observed in the wavelength resolved anisotropy measurements. 1) A strong bleach is observed at 800 nm due to B^* excitation and depletion of ground state B. This feature decays with sub-100 fs and 300 fs time constants. 2) A strong bleach at 860 due to bleaching of P_{y-}, which remains for tens of ps. When B alone is excited, the bleaching of P_{y-} grows in with a time constant of approximately 200 fs. 3) A broad excited state absorption at 770 nm due to P. This feature is present immediately after excitation of P*, decays with the electron transfer time, and exhibits oscillations

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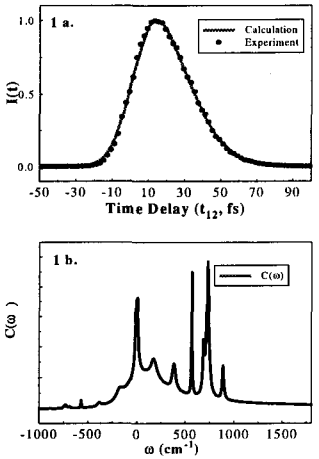
consistent with the special pair marker mode. Finally a bleach component at 820 nm which we have assigned to the P_{y+} transition. As with the excited state absorption from P_{y-}, this feature appears immediately after exclusive excitation of P_{y-} and yields anisotropy values consistent with an angle of 70° with respect to the P_{y-} transition. This transition moment is in agreement with low temperature results for P_{y+},[15,16] but the absorption wavelength is slightly further to the red. Upon excitation of B, this P_{y+} component shows a faster rise time than does the P_{y-} component, and then a subsequent decay. This leaves open the possibility that P_{y+} acts as an intermediate for energy transfer between B^* and P_{y-}.



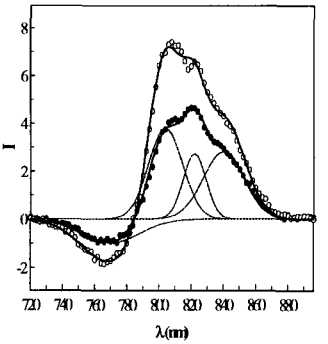


Figure Captions:

1. a) 2-pulse photon echo response of the accessory bacteriochlorophyll within the photosynthetic reaction center. points: experimental data, solid line: simulation. b) spectral density used to calculate the echo presented in 1a, as well as the linear absorption spectrum.

2. Parallel (open circles) and perpendicular (solid circles) wavelength resolved pump probe signals for a time delay of 200 fs after excitation of B*. Solid lines are fits to the data using four gaussian functions,which are are shown for the perpendicular data set (thin lines). Note, the spectra have NOT been corrected for the probe pulse laser spectrum. (80 nm FWHM centered at 800 nm).

References:

1. Fleming, G. R.; van Grondelle, R. *Phys. Today*, **1994**, (Feb) 48-55.
2. *The Photosynthetic Reaction Center*, Deisenhofer, J.; Norris, J. R. eds, Academic Press, 1993.
3. Kellog, E. C.; Kolaczkowski, S.; Waseliewski, M. R.; Tiede, D., *Photosynth. Res.*, **1989**, *72*, 47.
4. Chan, C. K.; DiMagno, T. J.; Chen, L. X. Q.; Norris, J. R.; Fleming, G. R. *Proc. Natl. Acad. Sci. USA*, **1991**, *88*, 11202.
5. Mukamel. S., *Nonlinear Optical Spectroscopy*, Oxford, **1995**.
6. Yang, T-S.; Vöhringer, P.; Arnett, D. C.; Scherer, N. F. *J. Chem. Phys.* ,**1995**, *103*, 8346.
7. Joo, T.; Jia, Y.; Fleming, G. R. *J. Chem. Phys.* **1995**, *102*, 4063.
8. Pshenichnikov, M. S.; Duppen, K.; Wiersma, D. A. *Phys. Rev. Lett.* **1995**, *74*, 674.
9. Wynne, K.; Hochstrasser, R. M. *Chem. Phys.* **1993**, *171*, 179.
10 Arnett, D. C.; Book, L. D.; Yang, T-S.; Scherer, N.F., *J. Chem. Phys.* submitted (1996).
11 Arnett, D. C.; Moser, C. C.; Book, L. D.; Dutton, P. L., Scherer, N. F., *J. Phys. Chem.* to be submitted (1996).
12 Small, G. *Chem. Phys.* **1995**, *197*, 239-257 and references therein.
13 Meech, S. R.; Hoff, A. J.; Wiersma, D. A., Chem. Phys. Lett. **1985**, *121*, 287.
14 Cherepy, N. J.; Shreve, A. P.; Moore; L. J. Franzen; S. Boxer, S. G.; Mathies, R. A. *J. Phys. Chem.* **1994**, *98*, 6023-6029.
15 Breton, *Biochim Biophys. Acta*, **1985**, *810*, 235-245.
16. Scherer, P.O.J.; Fischer, S. F.; Lancaster, C. R. D.; Fritzsch, G.; Schmidt, S.; Arlt, T.; Dressler, K.; Zinth, W., *Chem. Phys. Lett.* **1994**, *223*, 110-115.